The impact of volatile compounds released by paper on cellulose degradation in ambient hygrothermal conditions

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ABSTRACT

The reactivity towards cellulose of various volatile compounds commonly released by paper was studied. Sheets of Whatman No. 1 (W1) and No. 40 (W40) were exposed to various concentrations of these compounds in vapour phase ranging from 20 to 80 ppm in closed vessels for 52 days in controlled ambient conditions, after which they were hygrothermally aged. The measured properties of the paper were copper number, degree of polymerization, zero-span breaking length, pH and yellowness index. The results showed that hydrogen peroxide was the most aggressive among the volatile compounds tested as it severely degraded W1 cellulose. The exposure of W1 to formic acid led to significant degradation, designating this volatile organic compound (VOC) as the most reactive toward cellulose among the carboxyl and carbonyl functionalized VOCs tested. On the other hand, acetic acid was found comparatively less reactive. Nitrogen oxides, which were produced up to 3 ppm from a side-reaction of the carboxylic acids with the magnesium nitrate used to control the relative humidity in the closed vessels, appeared to contribute significantly to the degradation despite their low concentration. Antagonistic effects were evidenced in binary vapour mixtures where the presence of aldehydes (formaldehyde and acetaldehyde) counteracted substantially the degradation induced by the most reactive compounds. It was also shown that acetaldehyde, hexanal and furfural in individual exposures had little to no reactivity. Upon exposure to formaldehyde, the rate of glycosidic bond cleavage of cellulose induced by the ageing of W1 was significantly reduced.

1. Introduction

Notwithstanding recent developments, the research field of indoor air quality in heritage buildings is still in its infancy. Martin and Blades were among the first to report on the measurement of levels of volatile organic compounds (VOCs) inside museums in 1994 [1]. In 2003, an extensive review of the pollutants found in heritage institutions was conducted by Tétreault [2]. The bulk of this emerging research has largely been geared towards identifying and quantifying the pollutants in indoor air. The past decade, in particular, has seen a growing interest on the issue of indoor generated pollutants in libraries and archives. Recent studies have been devoted mostly to the measurement of VOCs in storage rooms housing paper-based collections, with a focus on carboxylic acids and aldehydes [3–6]. Research has also been dedicated to analysing

emissions from papers and books [7–18], as the main sources of VOCs in archival storage rooms are the paper-based items themselves. In view of the adverse contribution of off-gassing from paper collections to the indoor air quality, Ramalho et al. measured the emission rates of a selection of VOCs identified in various types of unaged and aged model papers and in naturally aged books [19].

To date, little is known on the potential damaging effect of the VOCs on cultural objects. Upon measuring the emission levels of acetic acid from typical archival cardboard storage boxes, Dupont and Tétreault [20] evaluated the deterioration of paper exposed to ppm levels of acid vapour, in terms of decrease in degree of polymerization of the cellulose. More recently, high temperature exposures to formic acid, 2-pentyl furan and NO_x at ppm levels were shown to unfavourably affect the degree of polymerization of cellulose in papers, while the effects of acetic acid were found to be more modest, and those of hexanal, furfural and formaldehyde were negligible on most papers [21,22]. Organic compounds with a high oxidative power such as hydroperoxides, the initial products in free radical autocatalytic oxidation, have been identified in pure

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cellulose paper [23–25]. Their presence was identified as free hydroperoxides cleaved from the cellulose chain as well as hydroperoxide functionalized cellulose, and their adverse impacts on cellulose degradation were quantified [24,25]. Hydroperoxides are also known to cause discolouration of black and white photographic prints [26,27]. Using Russell-effect images, Strlič et al. [28] were able to demonstrate that high levels of hydrogen peroxide (H_2O_2) were produced in aged papers containing iron-gall ink. Despite this new knowledge, there are still gaps concerning the effects of VOCs on paper and cellulose-based materials in typical indoor environmental conditions.

The present research aims to identify the volatile compounds that can induce or initiate deterioration in cellulose, and to simulate their long-term effects on the stability of paper using artificial ageing. Unlike other investigations, the exposures were carried out in ambient conditions in order to observe possible damage in real time, as well as to avoid initiating chemical processes that can take place at elevated temperatures. Hygrothermal ageing was performed after a desorption period of 10 days following the exposures.

Two pure cotton cellulose papers were used: Whatman No. 1 (W1), with a high molar mass, neutral pH and negligible initial oxidation level, and Whatman No. 40 (W40), a lower molar mass, pre-oxidized and more acidic paper. In 'Phase I' of the research, the papers were exposed to individual volatile compounds commonly released by paper. These were acetaldehyde, acetic acid, formaldehyde, formic acid, furfural, hexanal and hydrogen peroxide. However, real situations are complex as they bring simultaneously into play a number of volatile compounds, which are both released and absorbed by paper, depending on environmental and intrinsic parameters. For instance, during hygrothermal ageing, cross-contamination from paper or cellulose-based storage materials to neighbouring paper has been observed [29]. Air chemistry can also take place, and new volatile compounds can arise from reactions between different volatile compounds. Since it is not possible to test all conceivable combinations of volatile compounds, in 'Phase II' of the research, the synergistic and/or antagonistic effects of exposures to binary mixtures of volatile compounds were assessed in an attempt to model real exposure situations. These combinations included two compounds, which had been identified in Phase I as highly reactive and less reactive at ambient temperature, respectively. The impact of exposures where adventitious nitrogen oxides (NO_x) were additionally present was also investigated.

Previous studies have evaluated the migration of VOCs internally generated in stacks of paper [30,31] and the migration of outdoor pollutants such as sulphur dioxide through papers [32] and cardboard [33]. To simulate paper sheets in a closed book this research also examined the migration of volatile compounds through stacks of paper from the edges inward at ambient conditions.

2. Experimental

2.1. Chemicals

Acetaldehyde (99%), formaldehyde (37%), furfural (99%) and hexanal (98%) were purchased from Sigma–Aldrich. Acetic acid glacial, formic acid (88%), magnesium nitrate hexahydrate and sodium chloride were from Fisher Scientific. Hydrogen peroxide (30%) was obtained from J.T. Baker.

2.2. Generation and measurement of specific vapour phase environments

A three component system of volatile compound–water–salt was used. This system is based on the equilibrium of water vapour with a saturated salt mixture and the equilibrium of a volatile compound between its vapour and liquid phases. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and sodium chloride (NaCl) were used to generate a relative humidity (RH) of 54% and 75% at ambient temperature, respectively [34]. Aqueous solutions (40 ml) of the volatile compounds at different concentrations were mixed with 100 g of salt and placed in airtight 9 L Pyrex desiccators (200 mm i.d.). The presence of volatile compounds does not modify the RH in the desiccators, as shown in previous research [35]. Since hexanal is not water soluble, pure hexanal (0.1 ml) was deposited inside the desiccator, adjacent to the water/salt solution. For the binary compounds exposures, the solutions were poured into separate beakers and placed in the desiccator (20 ml and 50 g of salt each). Control samples were produced by exposing paper to the water/salt mixture only. The volatile compounds used and the environmental conditions are listed in Tables 1 and 2.

Measurements of the volatile compounds in the headspace of the desiccators were carried out with Dräger and Gastec detector tubes. According to the suppliers, the relative standard deviations (RSD) on the quantitation are 5%, except for formic acid (RSD 15–10%) and formaldehyde (RSD 20–15%). The measurement of hexanal had to be done with the tubes designed for acetaldehyde measurement as commercial hexanal-dedicated tubes were not available. The conversion for the concentration calculation was done as follows. At saturation, hexanal generates 2000 ppm in the headspace, which yielded a measurement of 26 ppm (equivalent) acetaldehyde. The level of hexanal was then calculated as 77 ($\sim$2000/26) times the level of acetaldehyde measured assuming a linear relationship.

Three air sampling measurements were made in each desiccator containing the paper samples: once the equilibrium was reached, a few days after the beginning of the exposure, and again at the end

Table 1
Exposure conditions of W1 in the temperature range 20.6–21.6 °C.

Volatile compounds	Solution's concentration (vol/vol %)	RH during exposure (%)	Average concentration in air with papers (ppm)
Water (control)	100	54	
Water (control)	100	75	
Acetaldehyde (Ac)	0.017	54	60 ± 4
Acetic acid (AA)	2.17	54	AA: 41 ± 4, NO$_x$: 0.5
Acetic acid	2.17	54	AA: 37 ± 4, NO$_x$ < 0.5
Acetic acid	2.17	75	67 ± 9
Acetic acid	1.00	75	28 ± 4
Formaldehyde (F)	1.98	54	30 ± 5
Formaldehyde	1.98	75	19 ± 5
Formic acid (FA)	3.04	75	38 ± 9
Furfural	1.14	54	82 ± 8
Hexanal	0.10 ml[a]	54	810 ± 280[b]
Hydrogen peroxide (H_2O_2)[c]	30	75	H_2O_2: 30, F < 1, FA: 3[d]
Acetaldehyde + acetic acid	0.012, 4.30	54	Ac: 91 ± 8, AA: 40 ± 4, NO$_x$: 3 ± 1
Formaldehyde + formic acid	3.90, 3.77	75	57 ± 6, 28 ± 5
H_2O_2 + formaldehyde[c]	30, 4.00	75	H_2O_2 < 1, F: 16, FA: 41[d]
H_2O_2 + formaldehyde without papers[c]	30, 4.00	100	H_2O_2 < 1, F: 31, FA: 20

[a] 0.1 ml of hexanal 98% in separate beaker (not mixed with water-salt solution).
[b] Measured with acetaldehyde detection tube.
[c] Average vapour concentration based on integration of polynomial fit curve.
[d] Detection made with formic acid tubes.